PH SENSITIVE PHOTOCHROMIC DYES

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Inventor: CLARKE DAVID A (GB); HERON BERNARD MARK (GB); GABBUTT CHRISTOPHER DAVID (GB); HEPWORTH JOHN DAVID (GB); PARTINGTON STEVEN MICHAEL (GB); CORNS STEPHEN NIGEL (GB)

Applicant: JAMES ROBINSON LTD (GB); CLARKE DAVID A (GB); HERON BERNARD MARK (GB); GABBUTT CHRISTOPHER DAVID (GB); HEPWORTH JOHN DAVID (GB); PARTINGTON STEVEN MICHAEL (GB); CORNS STEPHEN NIGEL (GB)

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Abstract of **WO9931081**

Naphthopyrans of formula (I) or (II) reversibly change their optical properties (colour, induced optical density and/or colourability) with changes of pH. In the formulae, R<1> and R<2> are hydrogen or certain hydrocarbyl or heterocyclic groups, R<3> is an amino functional group or certain oxygen, sulphur or phosphorus groups; and R<4> may be certain C1-C20 linear or branched alkoxy or alkyl (substituent) groups or is chosen from R<1>, R<2> or R<3>; and each n is 0 or 1 to 6, the total of all n's being no more than 6.

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(71) Applicant *(for all designated States except US)*: JAMES ROBINSON LIMITED [GB/GB]; Hillhouse Lane, P.O. Box 83, Huddersfield HD1 6BU (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CLARKE, David, A. [GB/GB]; 23 Wentworth Court, Rastrick, Brighouse HD6 3XD (GB). HERON, Bernard, Mark [GB/GB]; 63 Welton Road, Brough, East Riding, Yorkshire HU15 1AB (GB). GABBUTT, Christopher, David [GB/GB]; 7 New Row, Knowle Green, Preston, Lancashire PR3 2YS (GB). HEPWORTH, John, David [GB/GB]; 2 Carnoustie Close, Fulwood, Preston, Lancashire PR2 7ER (GB). PARTINGTON, Steven, Michael [GB/GB]; 48 Woodroyd, Golcar, Huddersfield HD7 4PG (GB). CORNS, Stephen, Nigel [GB/GB]; 10 Beech Street, Paddock, Huddersfield HD1 4JN (GB).

(74) Agents: WAIN, Christopher, Paul et al.; A.A. Thornton & Co., Northumberland House, 303–306 High Holborn, London WC1V 7LE (GB).

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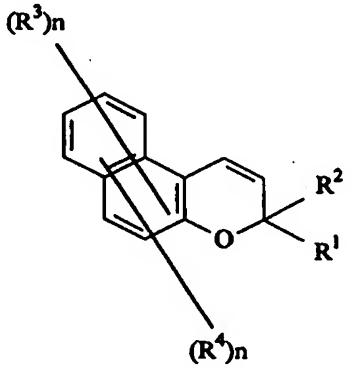

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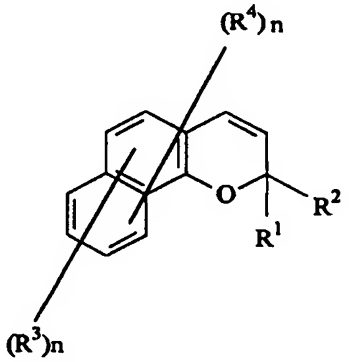

(II)

(57) Abstract

Naphthopyrans of formula (I) or (II) reversibly change their optical properties (colour, induced optical density and/or colourability) with changes of pH. In the formulae, R^1 and R^2 are hydrogen or certain hydrocarbyl or heterocyclic groups, R^3 is an amino functional group or certain oxygen, sulphur or phosphorus groups; and R^4 may be certain C_1–C_{20} linear or branched alkoxy or alkyl (substituent) groups or is chosen from R^1, R^2 or R^3; and each n is 0 or 1 to 6, the total of all n's being no more than 6.

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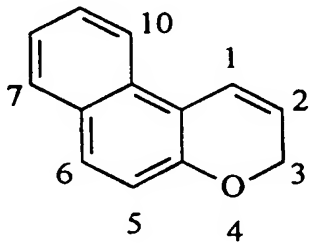
PH SENSITIVE PHOTOCHROMIC DYES

The present invention relates to photochromic dyes.

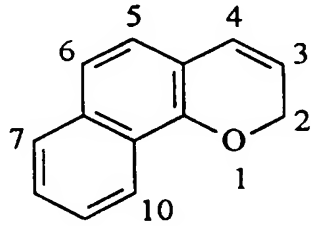
Photochromism is a well-known physical phenomenon and has been detailed in "Photochromism: Molecules and Systems" Studies in Organic Chemistry, 40, Eds. H. Dürr and H. Bouas-Laurent, Elsevier, 1990. Similarly, the phenomenon of pH sensitive dyes/indicators and stains is well established; (see, for example, 'Colour Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments'; H. Zollinger, VCH (Germany) 1991).

The 3*H*-naphtho[2,1-*b*]pyran and 2*H*-naphtho[1,2-*b*] pyran systems are known to be capable of exerting a photochromic effect (see, for example, Y. Hirshberg and E. Fischer, J. Chem. Soc., 1954, 3129 and R. Livingstone *et al.*, J. Chem Soc., 1958, 2422).

The basic 3*H*-naphtho[2,1-*b*]pyran and 2*H*-naphtho[1,2-*b*] pyran structures are illustrated below:



3*H*-naphtho[2,1-*b*]pyran



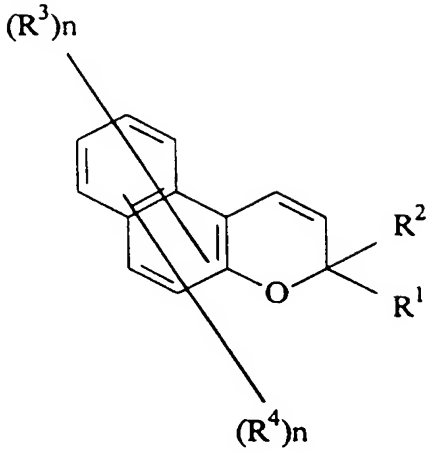
2*H*-naphtho[1,2-*b*]pyran

The photochromic properties of both the 3*H*-naphtho[2,1-*b*]pyran and 2*H*-naphtho[1,2-*b*]pyran systems have been intensively studied. For examples of 3*H*-naphtho[2,1-*b*]pyrans, see US patent 4,826,977 (1989), US patent 5,066,818 (1991), PCT WO 91/00861 (1991), PCT WO 92/01959 (1992), PCT WO 92/09593 (1992), PCT WO 94/22850 (1994), PCT WO 95/00866 (1995), US patent 5,532, 361 (1996), US patent 5,520,853 (1996), US patent 5,552,090 (1996) and PCT WO 97/06455 (1997); and for examples of 2*H*-naphtho[1,2-*b*] pyrans, see EP patent 0,250, 193 (1987), US patent 4,818,096 (1989), US patent 5,066,818 (1991), Research Disclosures Pilkington PLC (1992/3), US patent 5,458,814 (1995) and US patent 5,514,817 (1996).

We have now found that changing the pH of a solution, matrix or host material containing certain photochromic dyes can affect the spectroscopic properties, namely those of colour (λ_{max}), induced optical density and colourability of the incorporated photochromic dye. Significant shifts in the colour (λ_{max}) together with enhanced induced optical density and improved colourability can be observed without any apparent change in the rate of colouration, though the rate of fade (bleaching) may be altered. This effect is fully reversible and hence provides a means of switching the spectroscopic properties of a photochromic dye by adjusting the pH of its environment. Reversion to the original form of the photochromic dye by adjustment of the pH of its environment results in the return of its associated photochromic properties.

We have further found that, for this new effect to operate, certain structural features of the photochromic molecule are essential, in particular the aromatic moiety of the photochromic dye must have directly bonded to it at least one pH sensitive functional group. Such functional group(s) must contain either (i) one or more 'lone pairs' of electrons that may be reversibly protonated or (ii) one or more acidic protons that may be reversibly removed by the action of a base.

The photochromic dyes of the present invention are naphthopyrans of formula I or II:



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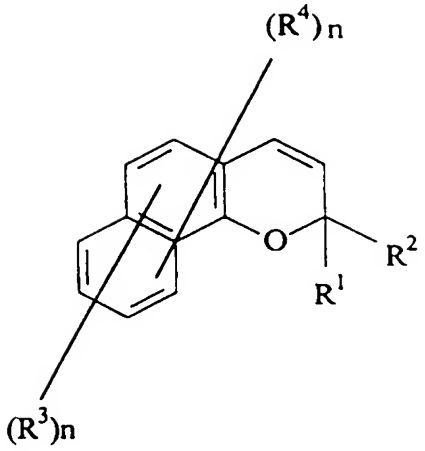
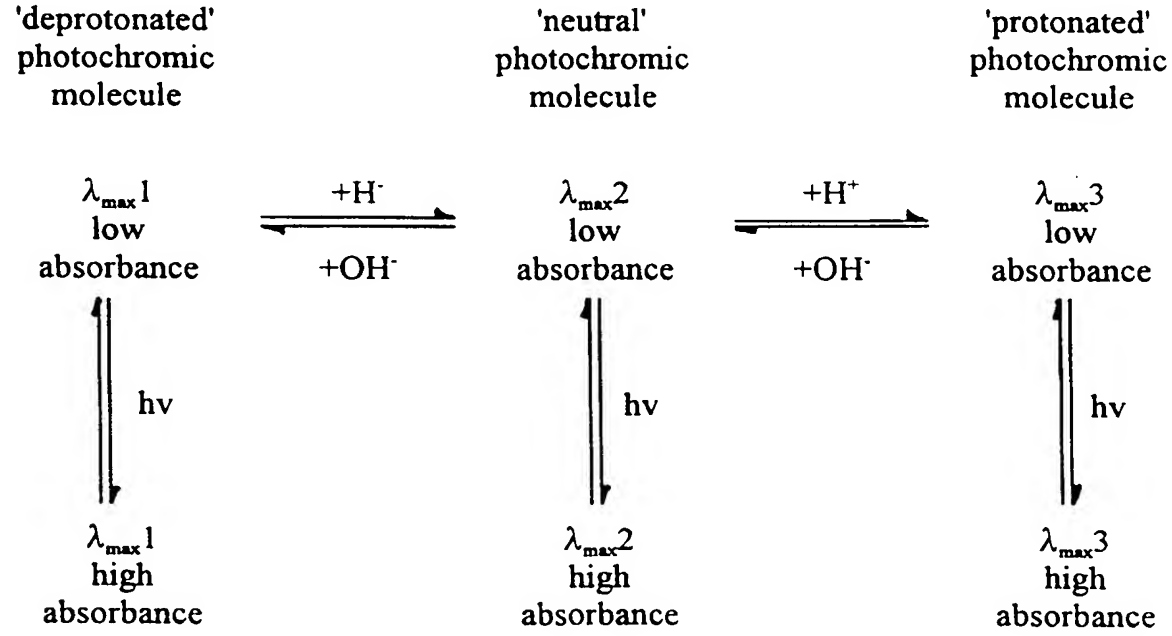


(II)

wherein R^1 and R^2, which may be the same or different, are each H, an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkynic group, a substituted alkynic group, a cycloalkyl group, a substituted cycloalkyl group, a heterocycloalkyl group, a substituted heterocycloalkyl group, a cycloalkenyl group, a substituted cycloalkenyl group, an aryl group, a naphthyl group, or a heteroaryl group and their substituted derivatives; R^1 and R^2 may be conjoined to form a ring, for example but not exclusively, cyclopentane, indane, indene, dibenzosuberane, dibenzosuberene, fluorene, xanthene, thioxanthene, acridine and their substituted derivatives particularly alkoxy and amino derivatives as defined below for R^3; the or each R^3 which may be the same or different is amino, C1-C20 linear or branched alkylamino, C1-C20 linear or branched dialkylamino, C3-C20 cycloalkylamino, C3-C20 substituted cycloalkylamino, C3-C20 cycloalkyl C1-C20 linear or branched alkylamino, C3-C20 substituted cycloalkyl C1-C20 linear or branched alkylamino, C3-C20 dicycloalkylamino, C3-C20 substituted dicycloalkylamino, C3-C20 cycloalkyl arylamino, C3-C20 substituted cycloalkyl arylamino, C1-C20 linear or branched alkyl arylamino, arylamino, diarylamino, cyclic amino for example but not exclusively aziridino, azetidino, pyrrolidino, piperidino, homopiperidino, perhydroazocino, piperazino,

N-alkylpiperazino, N-arylpiperazino, morpholino, thiomorpholino, their substituted derivatives and their mono and di benzologues; aminoaryl in which the amino function is defined as above for R^3, bridgehead aminoaryl units such as julolidine and lilolidine; hydroxy, hydroxyaryl, thiol, mercaptoaryl, carboxylic acid, thiocarboxylic acid, sulfur and phosphorus based acids. In the above definition, the terms cycloalkyl and substituted cycloalkyl include bi and tri cycloalkyl amino and substituted derivatives; the or each R^4 which may be the same or different is C1-C20 linear or branched alkoxy, C1-C20 linear or branched alkylthio, alkylsulfinyl, alkylsulfonyl, arylsulfinyl, arylsulfonyl, halogen, nitro, nitrile, formyl, acyl, aroyl, acetamido, C2-C10 N-alkylamido, alkoxycarbonyl, aryloxy, arylthio, or is selected from those atoms and groups specified above for R^1, R^2 and R^3; and each 'n' is 0 or an integer from 1 to 6 provided that in any one compound the total of all 'n's is not more than 6.

The effect of a change in pH may be conveniently illustrated by the scheme below:



The photochromic and pH colour switching properties exhibited by the pyran compounds of the present invention render these compounds particularly

useful as photochromic/pH sensitive indicators, inks, paints, varnishes and stains for 'printing' onto paper and fabrics and other surfaces e.g. glass, plastics and metals. This latter application may be particularly useful for the preparation of security markers (labels) on a broad range of objects e.g. cheques, bonds, bankers drafts, credit cards, charge cards and identity documents and cards and discrete windows. Such inks and other like formulations may also be used for printing documents and greetings cards. The security/identity uses of these pH sensitive photochromic compounds and formulations containing them may also extend to include the marking of fuels e.g. petrol and diesel and other oils.

Furthermore, the materials may be used in sensors, opto-chemical transducers, optical data recording systems e.g. compact discs, and read/write optical data storage discs, as waveguides and laser dyes.

Alternatively, these compounds may be incorporated into polymeric or sol-gel or colloidal type host materials so as to impart photochromic and pH colour switching properties to the said host materials.

Examples of applications of the polymeric host materials of the present invention include the manufacture of lenses for sunglasses and ophthalmic lenses, protective visors, screens, films, 'plastic' sheeting, containers (e.g. bottles and other packaging vessels), mirrors, windows and screens for vehicles such as cars (including sunroofs), motorcycles, aircraft and ships, architectural uses e.g. glazing, and artistic 'stained glass' windows and for use in novelty items. Additionally the materials may be used in vehicle body panels including fairings

and spoilers, and related external surfaces and other embodiments where it may be deemed attractive to have said objects change colour in the presence of sunlight.

The photochromic pyrans of the present invention may be incorporated into the 'plastic' host material by well established protocols for example as described in European Patent No. 0254020 or U.S. Patent No. 5,066,818.

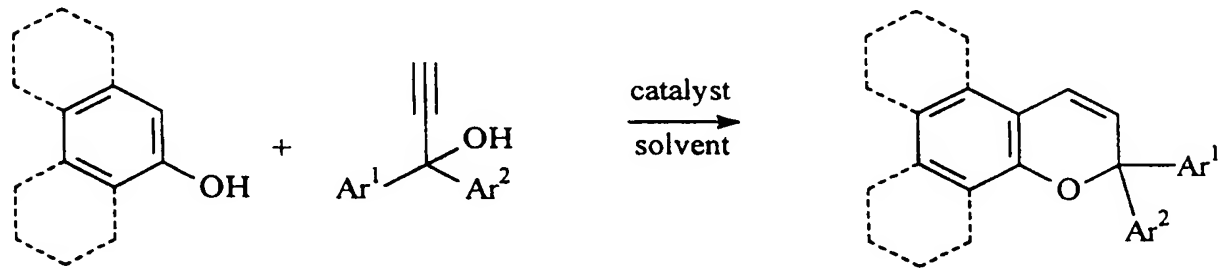
Typical host materials may include optically clear polymer materials, such as polymers of polyol (allyl carbonate) - monomers, polyacrylates such as polymethylmethacrylates, cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), polyuretanes, polycarbonate, polyethylene terephthalate, polystyrene, poly(triethyleneglycol dimethylacrylate), poly(diethyleneglycol bis(allyl carbonate)) and various copolymer mixes.

The pH colour switching ability is particularly useful in that a single manufactured photochromic dye may be used to impart different colours to a solution, matrix or host material depending upon the pH of the solution, matrix or host material.

The high induced optical density and enhanced colourability of these photochromic compounds of the present invention enables the amount of the photochromic material required so as to impart a useful degree of photochromism to a polymeric host material or to a solution to be greatly reduced, thereby enabling a considerable saving of synthetic effort and cost. Furthermore, the use of reduced

quantities of the photochromic materials of the present invention has the bonus that there is a consequent reduction in any undesirable colour that the photochromic materials may impart in the bleached state either by way of inherent colour of the material itself or by the formation of coloured fatigue/degradation products through use of the photochromic material.

The naphthopyrans of the present invention maybe prepared by a general method which is based on the following reaction scheme:



This general synthetic methodology has been described, for example by L. Merlini in 'Advances in Heterocyclic Chemistry,' 1975, vol. 18, page 159, and by R. Guglielmetti in "Photochromism: Molecules and Systems," Studies in Organic Chemistry 40, chap. 8, Eds. H Dürr and H. Bouas-Laurent, Elsevier, 1990, and also in several patent documents, for example WO 94/22850 and U.S. Patent No. 5,520,853 (1996). The synthesis of the propargyl alcohols shown in the scheme above are obtained in a known manner, for example, T. F. Rutledge in 'Acetylenic Compounds,' Reinhold, New York, 1968.

The substituted benzophenones required for the synthesis of the propargyl alcohols are either commercially available or obtained by documented

procedures described in the literature e.g. B. M. Khadilkar *et al.* Tetrahedron Letters 1997, 38(9) 1641; J. P. Wolfe *et al.* Journal of Organic Chemistry, 1997, 62, 1264.

The 1- and 2-naphthols and related hydroxy compounds are either commercially available or obtained by known synthetic methods, or derived from such methods; see for example WO 94/22850, W. S. Johnson *et al.* Organic Reactions 1951, vol. 6; D. W. Cameron *et al.* Australian Journal of Chemistry, 1980, 33, 2531.

The catalyst may be selected, for example, from alumina, acetic acid, trifluoroacetic acid, aryl or alkyl sulfonic acids, silica, clays (e.g. montmorillionite, tonsil) or acidic exchange resins. Any suitable organic solvent can be used. Those frequently employed for the reaction include benzene, toluene, xylene and relatively high boiling alkanes, for example.

In the definition of the naphthopyrans of the invention given above, the term alkyl group means any linear or branched C1-C20 alkyl group and includes haloalkyl and perhaloalkyl groups. The term substituted alkyl group means any linear or branched C1-C20 alkyl group which is substituted in any position or positions with a functional group which contains the heteroatom nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms. Additionally, the substituted alkyl group may be taken to mean any linear or branched C1-C20 alkyl group which is substituted in

any position or positions with a functional group which contains one or more carbon atoms bonded to one or more of the heteroatoms nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms.

The term alkenyl group means any isomeric linear or branched C2-C20 alkenyl group and includes haloalkenyl and perhaloalkenyl groups and may contain one or more alkene bonds. The term substituted alkenyl group means any isomeric linear or branched C2-C20 alkenyl group which is substituted in any position or positions with a functional group which contains the heteroatom nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms. Additionally, the substituted alkenyl group may be taken to mean any isomeric linear or branched C2-C20 alkenyl group which is substituted in any position or positions with a functional group which contains one or more carbon atoms bonded to one or more of the heteroatoms nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms.

The term alkynic group means any linear or branched C2-C20 alkynic group and may contain one or more alkynic bonds.

The term cycloalkyl group, a substituted cycloalkyl group, a

cycloalkenyl group, and a substituted cycloalkenyl group include mono-, di-, tri- and tetracyclic C3-C20 containing systems and are defined as for their respective non-cyclic analogues.

The terms an aryl group and a naphthyl group refer to phenyl and 1- and 2-naphthyl groups, which are either unsubstituted or substituted with one or more of the same or different of the following substituents; halogen, C1-C6 linear or branched alkyl, C2-C6 linear or branched alkenyl, C2-C6 linear or branched alkynyl, phenyl, aryl, heteroaryl, C1-C6 linear or branched hydroxyl, C1-C6 linear or branched alkoxy, C1-C6 linear or branched alkylthio, alkylsulfinyl, alkylsulfonyl, amino, C1-C6 alkylamino, C1-C6 substituted alkylamino, C1-C6 dialkylamino, C1-C6 alkylarylamino, diarylamino, cyclic amino for example but not exclusively pyrrolidino, piperidino, homopiperidino, perhydroazocino, piperazino, *N*-substituted piperazino, morpholino thiomorpholino, indolino; nitro, carboxyalkyl, C1-C6 alkylcarbonyl, benzoyl, aroyl, heteroaroyl, formyl, nitrile, carboxyamido, or crown and aza crown systems.

The term a heteroaryl group means for example but not exclusively, any of the following heterocyclic systems and their mono- and di-benzologues and their mono- and di-naphthologues and their substituted derivatives bonded through any carbon or heteroatom possible: thiophene, furan, pyrrole, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, dithiole, triazole, tetrazole, pyran, thiopyran, pyridine, pyrimidine, pyridazine, pyrazine, oxazine and dithiin.

As used herein, the term alkoxy group means any linear or branched

C1-C20 alkoxy group and includes haloalkyloxy and perhaloalkyloxy groups, and the term substituted alkoxy group means any linear or branched C1-C20 alkoxy group which is substituted in any position or positions with a functional group which contains the heteroatom nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms. Additionally, the substituted alkoxy group may be any linear or branched C1-C20 alkoxy group which is substituted in any position or positions with a functional group which contains one or more carbon atoms bonded to one or more of the heteroatoms nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms.

As used herein, the term alkylthio group means any linear or branched C1-C20 alkylthio group and includes (as the alkyl part) haloalkyl and perhaloalkyl groups, and the term substituted alkylthio group means any linear or branched C1-C20 alkylthio group which is substituted in any position or positions with a functional group which contains the heteroatom nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms. Additionally, the substituted alkyl group may be any linear or branched C1-C20 alkylthio group which is substituted in any position or positions with a functional group which contains one or more carbon atoms bonded to one or more of the

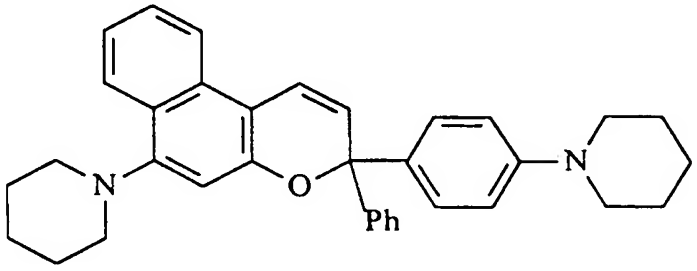
heteroatoms nitrogen or oxygen or sulfur or phosphorus or silicon, or any combination of two or more of the aforementioned heteroatoms, irrespective of the substituents directly bonded to said heteroatoms.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:

Example 1

(1) 6-Morpholino-3(4-piperidinophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran

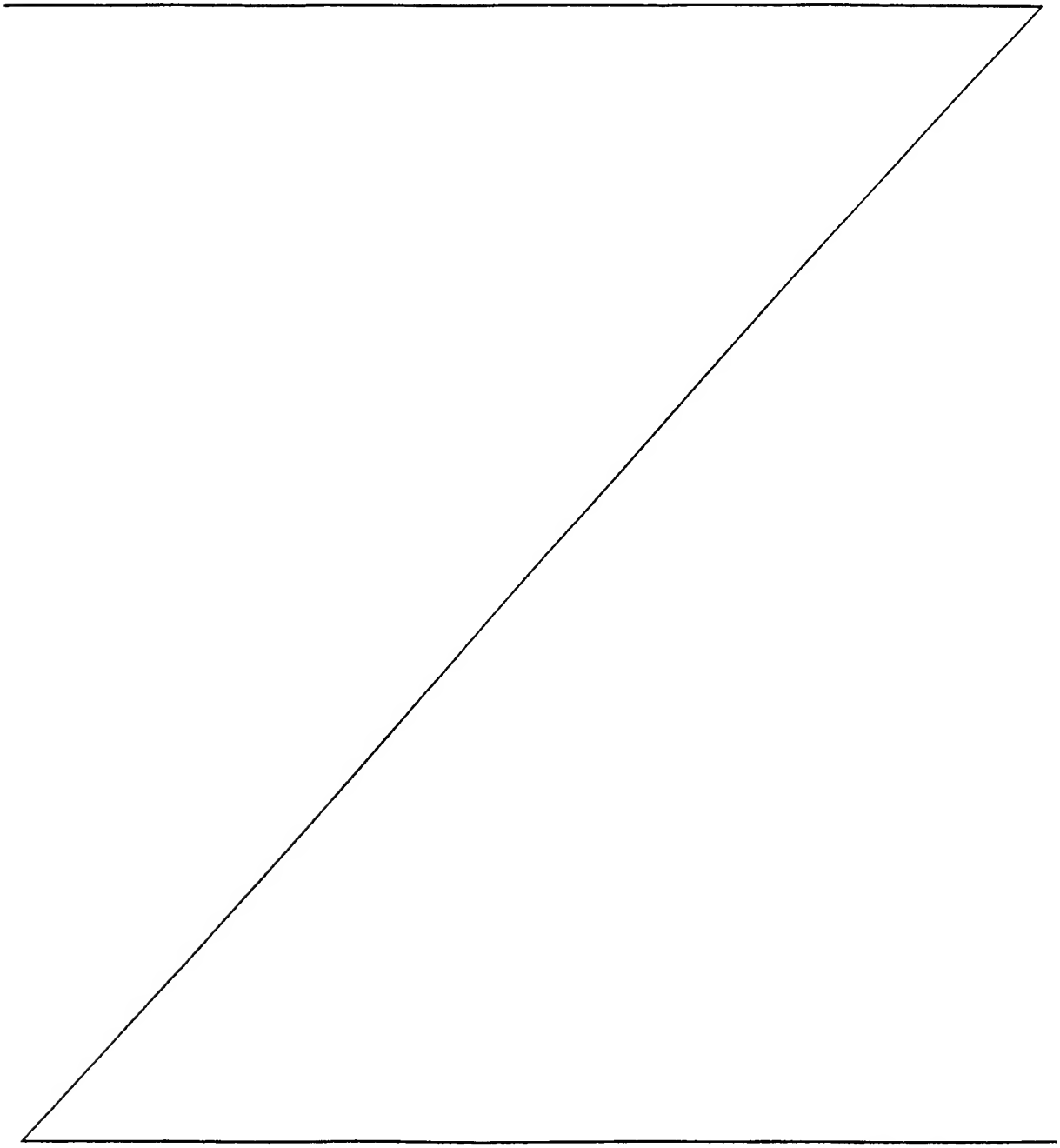
A solution of 4-morpholino-2-naphthol (6.5 mmol) and 1-(4-piperidinophenyl)-1-phenylprop-2-yn-1-ol (6.5 mmol) in toluene (65 cm^3) containing acidic alumina (Brockmann 1) (4.0g) was refluxed for 60 minutes. The cooled solution was filtered and the alumina was washed well with EtOAc (200 cm^3). Removal of the solvent from the filtrate gave an oil which solidified on standing at room temperature. Recrystallisation from EtOAc/hexane gave 6-morpholino-3(4-piperidinophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran (73%), m.p. = 170.5-172°C.

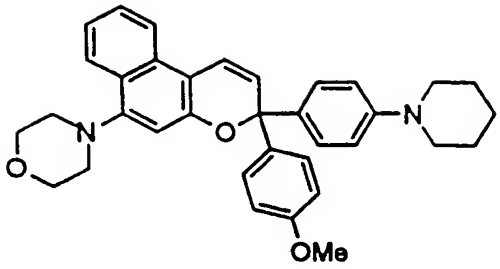


Examples 2 to 18

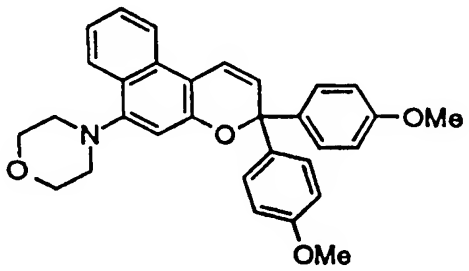
Following an identical protocol, but using the appropriate naphthol and prop-2-yn-1-ol, the following naphthopyrans were obtained:

(2) 3(4-Methoxyphenyl)-6-morpholino-3(4-piperidinophenyl)-3*H*-naphtho-[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1-(4-methoxyphenyl)-1-(4-piperidinophenyl)prop-2-yn-1-ol (75%) after recrystallisation from EtOAc, hexane and ethanol, m.p. = 247-249°C.

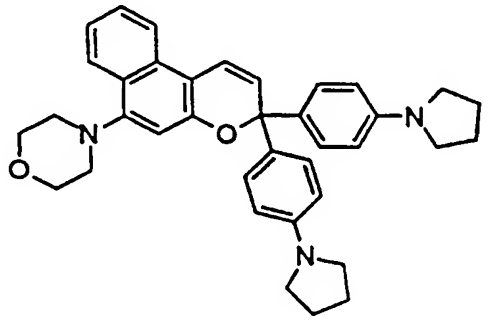




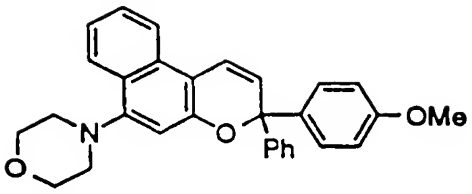
(3) 3,3-Di(4-methoxyphenyl)-6-morpholino-3*H*-naphtho[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (68 %) after recrystallisation from EtOAc, hexane and a trace of ethanol, m.p. = 211-213 °C.



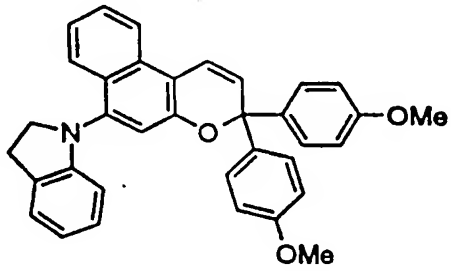
(4) 6-Morpholino-3,3-di(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1,1-di(4-pyrrolidinophenyl)prop-2-yn-1-ol (56 %) after recrystallisation from EtOAc and, m.p. = 243-245 °C.



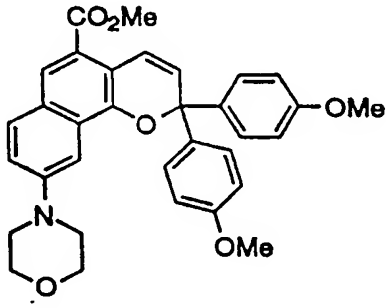
(5) 6-Morpholino-3-(4-methoxyphenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (71 %) after recrystallisation from hexane and a trace of EtOAc, m.p. = 164.5-165.0 °C).



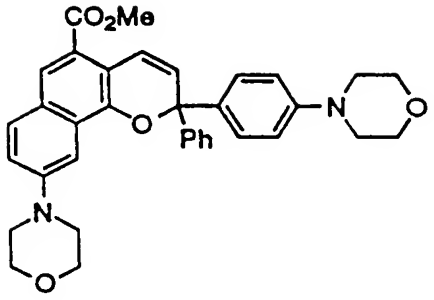
(6) 6-Indolino-3,3-di(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran from 4-indolino-2-naphthol and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (57 %) after recrystallisation from EtOAc and hexane, m.p. = 171-172 °C.



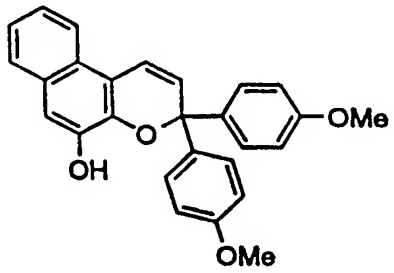
(7) Methyl 9-morpholino-2,2-di(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate from methyl 4-hydroxy-6-morpholinonaphthalene-2-carboxylate and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (42 %) after recrystallisation from EtOAc and hexane, m.p. = 153.5-155 °C.



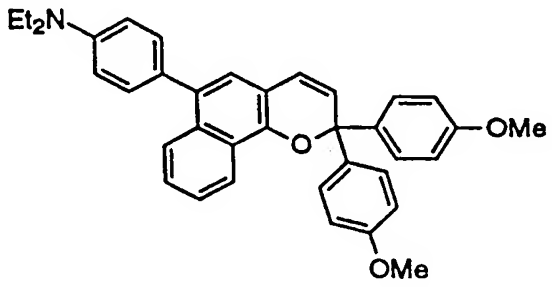
(8) Methyl 9-morpholino-2-(4-morpholinophenyl)-2-phenyl-2*H*-naphtho [1,2-*b*]pyran-5-carboxylate from methyl 4-hydroxy-6-morpholinonaphthalene-2-carboxylate and 1-(4-morpholinophenyl)-1-phenylprop-2-yn-1-ol (74 %) after recrystallisation from EtOAc and hexane, m.p. = 248-250 °C.



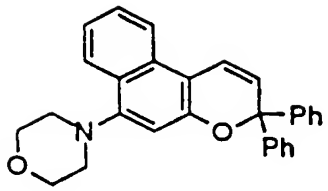
(9) 5-Hydroxy-3,3-di(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran from 2,3-dihydroxynaphthalene and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (53 %) after recrystallisation from EtOAc, hexane and a trace of ethanol, m.p. = 150.5-152 °C.



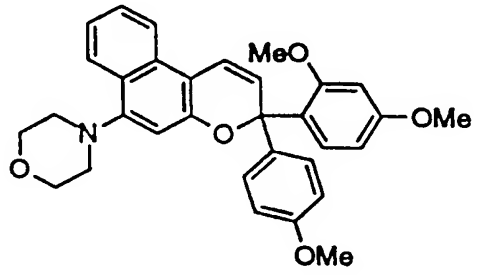
(10) 6-(4-*N*,*N*-Diethylaminophenyl)-2,2-di(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran from 4-(4-*N*,*N*-diethylanilino)-1-naphthol and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (61 %) after recrystallisation from EtOAc and hexane, m.p. = 147.5-149.5 °C.



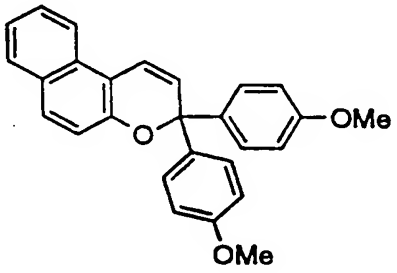
(11) 6-Morpholino-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1,1-diphenylprop-2-yn-1-ol (55 %) after recrystallisation from toluene and MeOH, m.p. = 187 -188 °C.



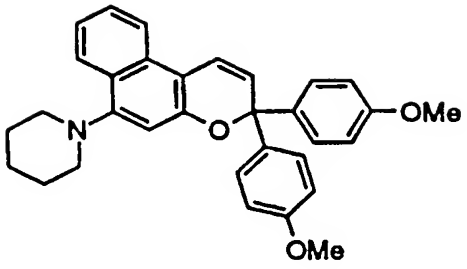
(12) 3-(2,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-6-morpholino-3*H*-naphtho[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (68 %) after recrystallisation from hexane and a trace of EtOAc, m.p. = 163-165 °C.



(13) 3,3-Di-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran from 2-naphthol and 1,1-di-(4-methoxyphenyl)prop-2-yn-1-ol (48 %) after recrystallisation from hexane and a trace of EtOAc, m.p. = 176-177 °C.



(14) 3,3-Di(4-methoxyphenyl)-6-piperidino-3*H*-naphtho[2,1-*b*]pyran from 4-piperidino-2-naphthol and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (73%) after recrystallisation from EtOAc, hexane and a trace of ethanol, m.p. = 114-119 °C.


N
O
OMe
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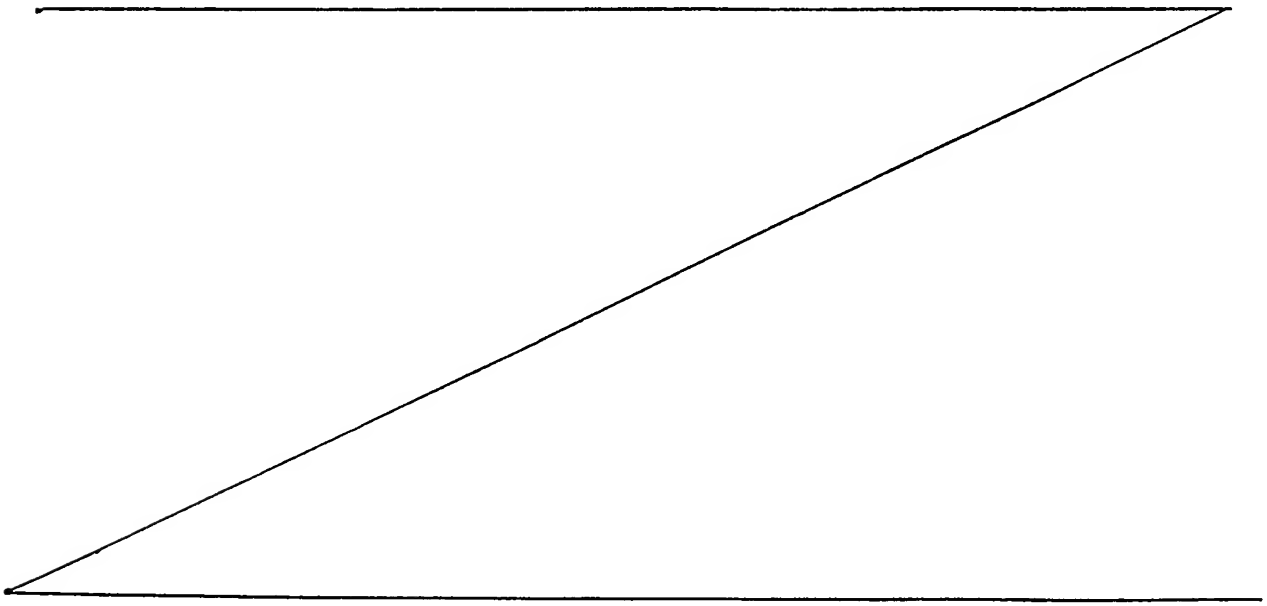
(15) 6-Morpholino-3(4-morpholinophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1(4-morpholinophenyl)-1-phenylprop-2-yn-1-ol (73%) after recrystallisation from EtOAc / hexane, m.p. = 187-188 °C.

(16) 6-Morpholino-3-phenyl-3(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran from 4-morpholino-2-naphthol and 1-phenyl-1(4-pyrrolidinophenyl)-prop-2-yn-1-ol (66%) after recrystallisation from EtOAc, hexane and a trace of ethanol, m.p. = 220-222 °C.

(17) 3,3-Di(4-*N*,*N*-dimethylaminophenyl)-6-morpholino-3*H*-naphtho[2,1-*b*]-pyran from 4-morpholino-2-naphthol and 1,1-di(4-*N*,*N*-dimethylamino-phenyl)prop-2-yn-1-ol (69%) after recrystallisation from EtOAc, hexane and a trace of ethanol, m.p. = 258.5-260.5 °C.

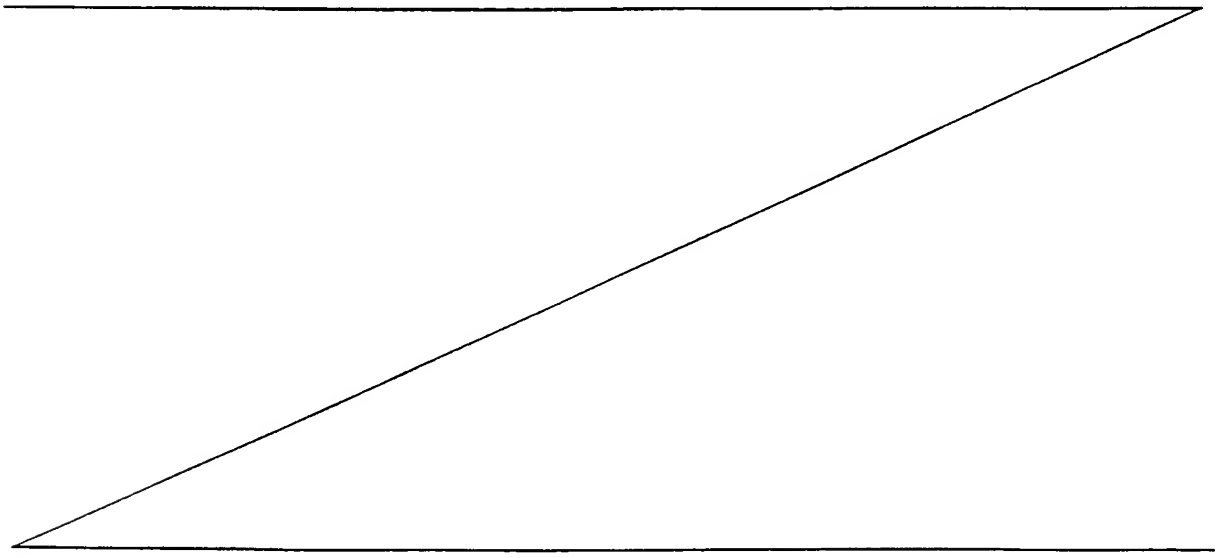
(18) 3,3-Di(4-*N*,*N*-diethylaminophenyl)-6-morpholino-3*H*-naphtho[2,1-*b*]-pyran from 4-morpholino-2-naphthol and 1,1-di(4-*N*,*N*-diethylamino-phenyl)prop-2-yn-1-ol (78%) after recrystallisation from EtOAc / hexane, m.p. = 235 -238 °C.



The photochromic properties of each of the naphthopyrans made in Examples 1 to 14 were measured and the results are set out in the following Table.

Compound reference		Neutral species		Modified species	
1		abs 0.10		abs 0.15	Δλmax 16
	λmax 482 nm		λmax 466 nm		
		abs* 1.59		abs* 2.51	

Compound reference		Neutral species		Modified species	
2		abs 0.19		abs 0.25	Δλmax 10
	λmax 484 nm		λmax 494 nm		
		abs* 1.63		abs* 2.34	



Compound reference		Neutral species		Modified species	
3		abs 0.08		abs 0.42	Δλmax 96
	λmax 438 nm		λmax 534 nm		
		abs* 0.95		abs* >3.5	

Compound reference		Neutral species		Modified species	
4		abs 0.31		abs 0.28	Δλmax 146
	λmax 538 nm		λmax 684 nm		
		abs* 0.58		abs* >3	

Compound reference		Neutral species		Modified species	
5		abs 0.04		abs 0.21	Δλmax 80
	λmax 426 nm		λmax 506 nm		
		abs* 2.48		abs* >3	

Compound reference		Neutral species		Modified species	
6		abs 0.01		abs 0.02	Δλmax 140
	λmax 464 nm		λmax 604 nm		
		abs* 0.33		abs* 0.64	

Compound reference		Neutral species		Modified species	
7		abs 0.01		abs 0.01	Δλmax 74/18
	λmax 442/534 nm		λmax 516 nm		
		abs* 0.50/0.43		abs* 0.10 (cold)	

Compound reference		Neutral species		Modified species	
8		abs 0.01		abs 0.01	Δλmax 14/84
	λmax 478/548 nm		λmax 464 nm		
		abs* 0.72/0.83		abs* 0.61	

Compound reference		Neutral species		Modified species	
9		abs 0.06		abs 0.16	Δλmax 20
	λmax 474 nm		λmax 454 nm		
		abs* 0.52		abs* 1.51	

Compound reference		Neutral species		Modified species	
10		abs 0.06		abs 0.10	Δλmax 46
	λmax 544 nm		λmax 498 nm		
		abs* 1.63		abs* 2.63	

Compound reference		Neutral species		Modified species	
11		abs 0.03		abs 0.08	Δλmax 64
	λmax 410 nm		λmax 474 nm		
		abs* >2		abs* >2.5	

Compound reference		Neutral species		Modified species	
12		abs 0.16		abs 0.23	Δλmax 90
	λmax 440 nm		λmax 530 nm		
		abs* 2.52		abs* >3	

Compound reference		Neutral species		Modified species	
13		abs 0.01		abs 0.02	Δλmax 0
	λmax 468 nm		λmax 468 nm		
		abs* 0.24		abs* 0.25	

Compound reference		Neutral species		Modified species	
14		abs 0.01		abs 0.10	Δλmax 84
	λmax 442 nm		λmax 526 nm		
		abs* 2.70		abs* 2.90	

NOTES

1. abs = absorbance of the photochromic dye in spectroscopic grade acetone prior to activation by a light source.

2. abs* = absorbance of the photochromic dye in spectroscopic grade acetone subsequent to activation by a light source.

3. All solutions are of a similar concentration *ca.* 1mmoldm^{-3}.

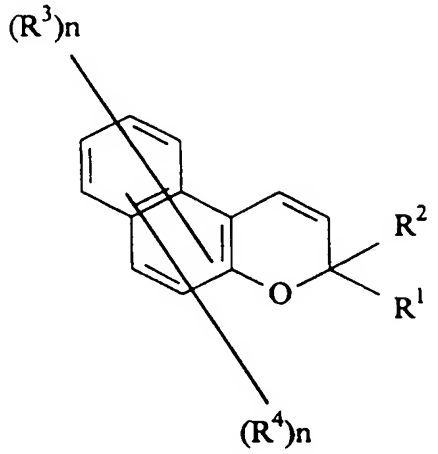
4. The irradiation sequence was identical for all solutions.

5. The term 'neutral species' refers to the photochromic dye prior to modification with acid or base.

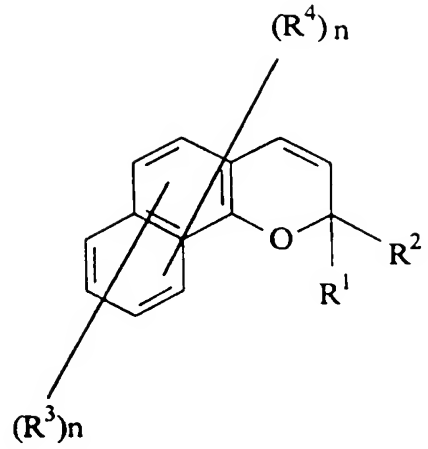
6. The term 'modified species' refers to the photochromic dye subsequent to treatment by acid or base.

CLAIMS:

1. A naphthopyran of the formula I or II:



(I)



(II)

wherein R^1 and R^2, which may be the same or different, are each H, an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkynic group, a substituted alkynic group, a cycloalkyl group, a substituted cycloalkyl group, a heterocycloalkyl group, a substituted heterocycloalkyl group, a cycloalkenyl group, a substituted cycloalkenyl group, an aryl group, a naphthyl group, or a heteroaryl group; R^1 and R^2 may be conjoined to form a ring which may be substituted; the or each R^3, which may be the same or different, is an amino function which is amino, C1-C20 linear or branched alkylamino, C1-C20 linear or branched dialkylamino, C3-C20 cycloalkyamino, C3-C20 substituted

cycloalkylamino, C3-C20 cycloalkyl C1-C20 linear or branched alkylamino, C3-C20 substituted cycloalkyl C1-C20 linear or branched alkylamino, C3-C20 dicycloalkylamino, C3-C20 substituted dicycloalkylamino, C3-C20 cycloalkyl arylamino, C3-C20 substituted cycloalkyl arylamino, C1-C20 linear or branched alkyl arylamino, arylamino, diarylamino, cyclic amino or a substituted cyclic amino derivative or a mono or di benzologue thereof; or aminoaryl in which the amino function is defined as above for R^3, or a bridgehead aminoaryl unit; or hydroxy, hydroxyaryl, thiol, mercaptoaryl, carboxylic acid, thiocarboxylic acid, sulfur or phosphorus based acid; and the or each R^4, which may be the same or different, is C1-C20 linear or branched alkoxy, C1-C20 linear or branched alkylthio, alkylsulfinyl, alkylsulfonyl, arylsulfinyl, arylsulfonyl, halogen, nitro, nitrile, formyl, acyl, aroyl, acetamido, C2-C10 N-alkylamido, alkoxycarbonyl, aryloxy, arylthio, or is selected from those atoms and groups specified above for R^1, R^2 and R^3; and each 'n' is 0 or an integer from 1 to 6 provided that in any one compound the total of all 'n's is not more than 6.

2. A naphthopyran according to claim 1, wherein R^1 and R^2 are conjoined to form a ring which is a substituted or unsubstituted cyclopentane, indane, indene, dibenzosuberane, dibenzosuberene, fluorene, xanthene, thioxanthene or acridine ring.

3. A naphthopyran according to claim 2, wherein the said ring is

substituted with at least one alkoxy or amino group.

4. A naphthopyran according to claim 1, 2 or 3, wherein R^3 is an amino function which is a cyclic amino group selected from aziridino, azetidino, pyrrolidino, piperidino, homopiperidino, perhydroazocino, piperazino, N-alkylpiperazino, N-arylpiperazino, morpholino and thiomorpholino.

5. A naphthopyran according to claim 1, 2 or 3, wherein R^3 is a bridgehead aminoaryl unit which is juloidine or lilolidine.

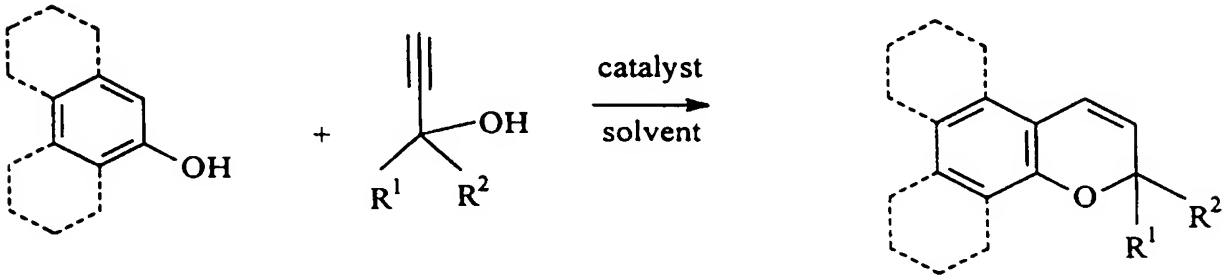
6. 6-Morpholino-3(4-piperidinophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran, 6-morpholino-3(4-morpholinophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran, 3(4-methoxyphenyl)-6-morpholino-3(4-piperidinophenyl)-3*H*-naphtho-[2,1-*b*]pyran, 6-morpholino-3(4-pyrrolidinophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran 3,3-di(4-methoxyphenyl)-6-morpholino-3*H*-naphtho[2,1-*b*]pyran, 6-morpholino-3,3-di(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran, 6-morpholino-3,3-di(4-*N,N*-dimethylaminophenyl)-3*H*-naphth[2,1-*b*]pyran, 6-morpholino-3,3-di(4-*N,N*-diethylaminophenyl)-3*H*-naphtho[2,1-*b*]pyran, 6-morpholino-3-(4-methoxyphenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran, 6-indolino-3,3-di(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran, methyl 9-morpholino-2,2-di(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate, methyl 9-morpholino-2-(4-morpholinophenyl)-2-phenyl-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate, 5-

hydroxy-3,3-di(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran, 6-(4-*N,N*-diethylaminophenyl)-2,2-di(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran, 6-morpholino-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran, 3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-6-morpholino-3*H*-naphtho[2,1-*b*]pyran, 3,3-di-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran and 3,3-di(4-methoxyphenyl)-6-piperidino-3*H*-naphtho[2,1-*b*]pyran.

7. A process for making a naphthopyran as defined in claim 1, which includes the step:

the above compounds including R^3 and/or R^4 substituents as desired in accordance with claim 1.

8. A process for making a naphthopyran as defined in claim 1



substantially as herein described in any of Examples 1 to 14.

9. An article, device or composition which comprises a naphthopyran

as claimed in claim 1, and a carrier therefor.

10. An article according to claim 9, wherein the carrier is a polymeric material.

11. An ophthalmic element which comprises a naphthopyran as claimed in claim 1.

12. The use of a composition according to claim 9 for labelling, printing, marking or painting.

13. The use of a composition according to claim 9, for characterisation, identification or security marking.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/GB 98/03681

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D311/92 C07D405/04 C09K9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 22850 A (PILKINGTON PLC ;RICKWOOD MARTIN (GB); SMITH KATHARINE EMMA (GB); G) 13 October 1994 see the whole document ---	1-13
X	US 5 552 090 A (KNOWLES DAVID B ET AL) 3 September 1996 see the whole document ---	1-13
X	GB 2 209 751 A (PLESSEY CO PLC) 24 May 1989 see claim 13 ---	1-3,7-13
X	US 5 650 098 A (KUMAR ANIL ET AL) 22 July 1997 see the whole document ---	1-4,7-13

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 February 1999	19. 02. 99

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,	Stoondijk, M

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/GB 98/03681

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 658 501 A (KUMAR ANIL ET AL) 19 August 1997 see the whole document	1-4,7-13
X	WO 95 00867 A (PPG INDUSTRIES INC) 5 January 1995 see the whole document	1-3,7-13
X	US 5 693 830 A (IMURA SATOSHI ET AL) 2 December 1997 see column 57 - column 58	1-3,7-10
X	WO 97 15565 A (RODENSTOCK OPTIK G ;ZINNER HERBERT (DE); MELZIG MANFRED (DE)) 1 May 1997 see the whole document	1-4,7-13
X	CHRISTIE R M ET AL: "An Investigation of the Electronic Spectral Properties of the Coloured Photoproducts Derived from Some Photochromic Naphtho[2,1 -b]pyrans" DYES AND PIGMENTS, vol. 35, no. 4, December 1997, page 339-346 XP004097396 see example 1E	1-4,6-13
X	WO 97 22895 A (PPG INDUSTRIES INC) 26 June 1997 see the whole document	1-3,7-13
A	US 3 627 690 A (CASELLA JOSEPH ET AL) 14 December 1971 see the whole document	1-13
P,X	EP 0 875 509 A (TOKUYAMA CORP) 4 November 1998 see the whole document	1-4,6-13
P,X	WO 98 42693 A (CORNS STEPHEN NIGEL ;GABBUTT CHRISTOPHER DAVID (GB); HEPWORTH JOHN) 1 October 1998 see examples 1-3	1-4,6-13
P,X	WO 98 45281 A (CORNS STEPHEN NIGEL ;GABBUTT CHRISTOPHER DAVID (GB); HEPWORTH JOHN) 15 October 1998 see examples 1-6	1-4,6-13

INTERNATIONAL SEARCH REPORT

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [X] Claims Nos.: 1-5,7-13 (all part)
because they relate to subject matter not required to be searched by this Authority, namely:

see FURTHER INFORMATION sheet PCT/ISA/210

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4 [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Claims Nos.: 1-5,7-13 (all part)

According to the description (page 2, 3rd paragraph) the compounds should be substituted in the aromatic moiety with at least one pH sensitive functional group. This is not reflected in the claims in which each n may be 0.
The search has been carried out in accordance with the teaching in the application that the aromatic moiety carries at least one pH sensitive functional group ("R3").

INTERNATIONAL SEARCH REPORT

.Information on patent family members

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